AN X-RAY STUDY OF UNIT CELL PARAMETER VARIATIONS IN LAUMONTITE AND LEONHARDITE

by

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I. INTRODUCTION

Laumontite ($CaAl_2Si_4O_{12}\cdot 4H_2O$) is a monoclinic, calcium-rich zeolite mineral, originally discovered in Brittany in 1785 by Gillet Laumont (Coombs, 1952). Noted for the ease with which it loses water, laumontite also occurs in a partially dehydrated form known as leonhardite ($Ca_2Al_4Si_8O_{24}\cdot 7H_2O$). The differences between the two phases appear to be only in small changes in the cell parameters and cell volume, but descriptions of the properties found in the technical literature are relatively unclear. Laumontite, and presumably leonhardite, typically occur as long, stout prismatic crystals in veins and cavities of crystalline rocks (Lapham, 1963). It is the purpose of this study to investigate changes in the cell parameters associated with the variation between laumontite and leonhardite.

Previous Work

One of the first technical papers involving an X-ray study of the laumontite-leonhardite relationship was prepared by D.S. Coombs in 1952 in which he determined cell parameters and volume changes associated with the two different phases. Due to limitations imposed on him by his equipment, however, he was unable to observe the (110) peak at a d-value of 9.49Å, which is listed as the principal peak in the X-ray powder data compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). In 1963, D.M. Lapham also prepared an X-ray study of laumontite in which he noted the principle (110) peak. The cell parameters derived by Lapham approximated those Coombs had observed previously, but Lapham did not study the effective volume changes (Table 1).

TABLE 1. Leonhardite cell parameters

	a.	b.	c.	β
Coombs (1952)	14.75Å+.05	13.08Å+.02	7.57Å+.05	112.0°+.02
Lapham (1963)	14.75Å+.03	13.10Å+.02	7.55Å+.01	112°

The purpose of this experiment was to test the reproduciability of the results obtained by Coombs and Lapham and to determine the amount of cell expansion upon hydration of leonhardite by means of X-ray diffraction measurements of powder specimens.

II. PROCEDURE

The specimen of laumontite used in this study is from the Ohio State University Mineralogy Museum and was collected in the Isle Royale National Park area, Michigan, where it occurs as a plagioclase replacement mineral in Precambrian basalt (Dorr and Eschman, 1970). The specimen was hand ground in a sintered alumina mortar and pestle and passed through a 53-micron sieve.

X-ray diffraction measurements were made using a Philips Electronic X-ray generator with copper K-alpha radiation, powder diffractometer, theta compensating slit, graphite monochromator, and recording panel. Operating conditions were 35 kilovolts, 15 milliamps, 1° two-theta per minute scan speed and 60 inches per hour chart speed.

Because the experiment involved samples which have a tendency to gain and lose water readily, it was necessary to provide a means by which the samples could be kept in the desired state during an X-ray diffraction experiment. For the dehydrated runs, a small container of commercial Drierite ($CaSO_4$) was placed inside the specimen chamber of the X-ray unit with the sample, which

had previously been thoroughly dried in a dessicator. For the hydrated runs, a relatively impermeable clear polyethylene film (0.0005" thick) was placed around the specimen holder which contained the hydrated sample. The only observed effect that the plastic film had on the diffraction pattern was the presence of a "plastic" peak at a d-value of 4.173Å or about 21.29° two-theta.

Diffraction patterns were measured of alternately wet and dry specimens to test the ease with which the mineral changed from laumontite to leonhardite and back again. After six runs were made, three each wet and dry, the peaks which could be unambiguously indexed were assigned Miller indices (hkl's) using information obtained from the JCPDS powder data file. The hkl's and corresponding two-theta positions were then used as input into a computer program for least-squares refinement of cell parameters.

Least-Squares Refinement of Cell Parameters

In the least-squares method of cell refinement, it is assumed that the valuable for which the sum of the squares of the residuals is to be minimized will be distributed randomly about its mean. Since the cell parameters are not linearly related to theta, a linear least-squares procedure minimizing residuals of $1/d^2$ can only be used to give a first approximation of the refined cell parameters. A subsequent non-linear program minimizing residuals of two-theta obtains the most probable cell parameters. The input and output for the computer program are as follows:

Input
(1) crystal system (Monoclinic)
(2) space group number (#8, International Tables for X-ray Crystallography, Vol.1)
(3) minimum d-spacing in Angstroms (1.344)
(4) observed hkl peaks and corresponding two-theta values (experimental data)

Output
(1) refined cell parameters of a, b, c, and β
(2) residuals of $1/d^2$ and two-theta
(3) computer generated list of all possible hkl peaks with corresponding d-values as a function of the new refined cell parameters

The possible hkl peaks the computer generated were dependent upon restrictions set by the mineral's crystal system and space group. Since laumontite is in space group Cm with monoclinic symmetry, systematic extinction only occurs when h+k is even. The program takes these conditions into account and lists all possible reflections under these space group restrictions.

In the monoclinic system, the distance between adjacent planes in the set (hkl) is given by the equation

$$\frac{1}{d^2} = \left(\frac{1}{\sin^2\beta} + \frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos\beta}{ac} \right)$$

Since this equation involves the four unknowns, a, b, c, and β, we would need, under optimum conditions, at least four independent observations to solve for the cell parameters. A solution based on only four reflections would most likely have a relatively large error, because there would be no redundant data against which the computer could check. In all cases, a minimum of no less than 8 peaks were initially used as input.

The resulting listing of possible peaks was then matched against the X-ray pattern in an attempt to identify those peaks which had previously been unindexed. Any newly indexed peaks

were then added as input to the refinement program. This procedure was repeated until all clearly discernable peaks were indexed.

III. DATA

The least-squares refinement proved to be quite helpful, both in indexing ambiguous peaks and in identifying those peaks which had been identified incorrectly. In several instances, peaks which do not show up on the JCPDS can be indexed using data from the computer generated listing. The JCPDS card may not include peaks with relatively low intensities, yet these peaks might have detectable intensities on the patterns of this study. The (110) peak which Coombs did not identify and which Lapham found to be the largest peak, does not occur as the largest in this study. On every pattern, the (130) peak at a d-value of 4.22Å is more intense, up to 40% greater on several of the leonhardite patterns.

In cases where the peaks are indexed incorrectly, the program shows a large value for the residual of two-theta, sometimes greater than .2 - .3%. This indicates that there was a large difference between the observed two-theta value of an hkl peak and the value calculated using the hkl information given. The computer generated hkl listing can then be cross referenced to find the correct hkl for the observed two-theta value.

Comparison to Previous Work

The values obtained for a, b, c, and β compare very well with those obtained in previous work, more favorably with Coombs' data after refinement, than with Lapham's. Although the data

presented by Coombs and Lapham compared favorably initially, upon refinement the values obtained by Lapham changed drastically. The cell parameters derived in this study are within about 2% of those obtained by Coombs and within about 6% of those obtained by Lapham (Table 2).

TABLE 2. Comparison of cell parameters of laumontite/leonhardite*

	this study		Coombs		Lapham**
	wet	dry	wet	dry	dry
a)	14.732Å±.02	14.634Å±.02	14.864Å±.05	14.798Å±.03	14.632Å±.37
b)	12.867Å±.03	13.084Å±.02	13.137Å±.02	13.081Å±.03	13.340Å±.32
c)	7.537Å±.02	7.548Å±.03	7.572Å±.02	7.583Å±.03	8.050Å±.66
β)	110.824°±.004	111.876°±.003	110.397°±.004	111.922°±.004	109.405°±.070

* Values for Coombs and Lapham have been refined using least-square program.
** No wet laumontite data was listed by Lapham

A point of significant difference in this study from that of Coombs is the expansion of the unit cell due to hydration. Coombs' sample cell volume increased an average of approximately 1.8% whereas the average expansion observed in this study was approximately 3.7% (Table 3).

TABLE 3. Comparison of cell volumes

	this study	Coombs
wet	1393.7287Å	1385.7799Å
dry	1341.8944Å	1361.7445Å
change	3.719%	1.734%

The theoretical volume change calculated from the chemical formulas is 1.91%. If the highest and lowest values for cell volume are discarded, the volume change observed in this study becomes 1.63% which is within about 6% of Coombs'.

Over the three cycles of hydration and subsequent dehydration which the sample underwent, no systematic changes or detri-

mental effects were noticed. The corresponding values obtained for cell parameters for each cycle were, except in one instance, within 0.15% of each other. The one set of values which differed greatly was that of a wet sample in which a large amount of specimen displacement was observed during the diffraction measurement, and which had been replaced with excess water prior to the experiment.

IV. CONCLUSIONS

As was the initial intention of this experiment, the values obtained by Coombs and Lapham proved to be quite reliable, with the obtained results agreeing more closely with Coombs. Although the specimen experienced a large volume increase, the average value for ΔV, not including the erroneous wet run is about 2.4%, which is different from Coombs' by about 25%. This error may be due to the differences in the two specimens or differences in the procedures used to obtain specimen hydration.

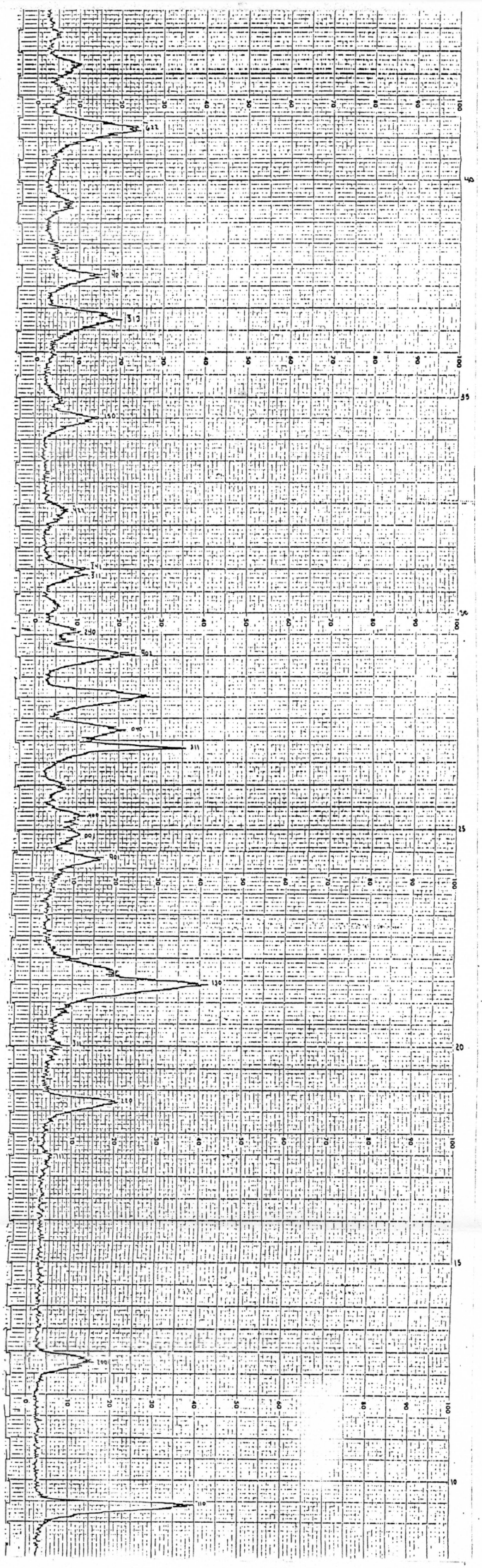

FIGURE 1.
Laumontite

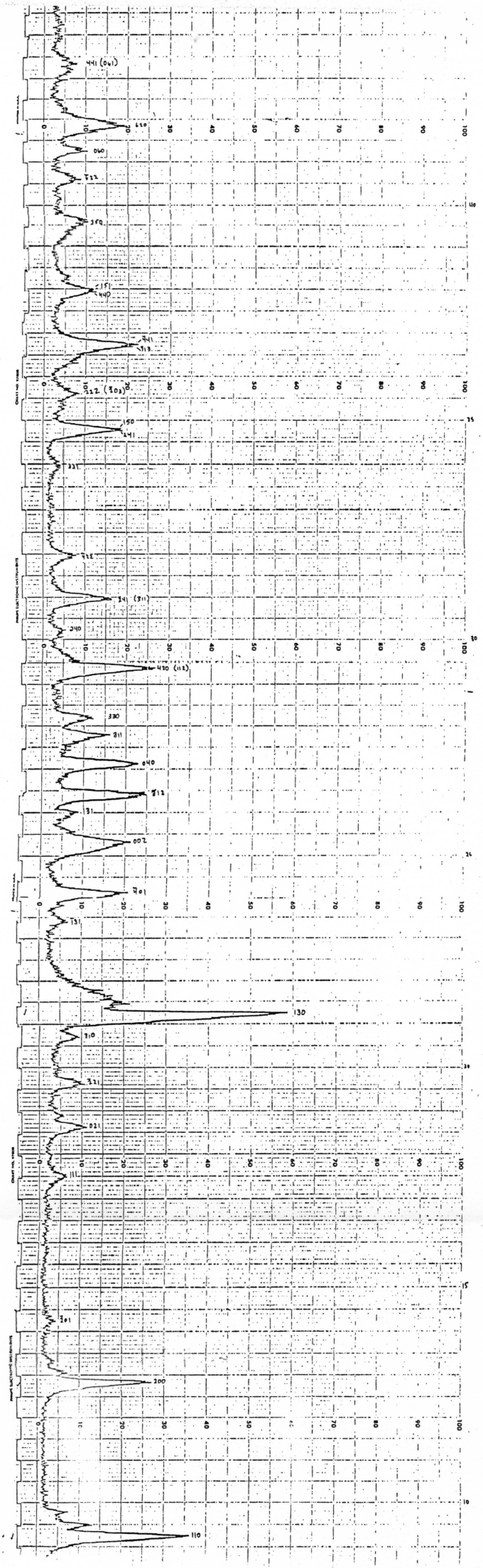

FIGURE 2.
Leonhardite

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